

those of the medullary cylinder. The bark of the fossil plants is compared with those of *Lycopodium chamæcyparissus* and *Selaginella Martensii*, which two combined represent the former.

These discoveries necessitate some changes in generic nomenclature, since the several parts of the plant not only represent the three genera above mentioned, but also several others. Meanwhile some other errors require correction. Corda erroneously defined his genus *Diploxyton* as having no medullary rays, and Brongniart relied upon this distinction in separating *Diploxyton* from *Sigillaria*; but no difference exists between the ligneous structures of the two genera, so far as *Sigillaria* is illustrated by Brongniart's *S. elegans*. Corda, Brongniart, and King all agree in regarding *Diploxyton* (which is identical with Witham's *Anabathra*) as belonging to the Gymnospermous Exogens. The necessity for abandoning this separation of the plants in question from the *Lycopodiaceæ*, urged in the author's previous memoir, is now made more obvious than before, the distinctions upon which the great French botanist relied in his classification being now shown to be such as mere differences of age can produce. The author concludes from his own observations that the genera *Diploxyton*, *Anabathra*, *Lomatophloios*, and *Leptoxyton* must be united. Brongniart had already brought into one generic group Corda's genera *Lomatophloios*, *Leptoxyton*, and *Calamoxylon*, Göppert's genus *Pachyphyllum*, and Sternberg's genus *Lepidophloios*, giving the latter name to the whole. Hence no less than six obsolete generic names are disposed of. The author finally follows Brongniart in adopting the term *Lepidophloios*, and temporarily assigns to the plant described the trivial name of *L. brevifolium*. The further relations of this genus to more ordinary forms of *Lepidodendron* require further investigation.

Much credit is due to G. Grieve, Esq., of Burntisland, for the energy with which he has worked amongst the deposits at Burntisland; and the author acknowledges his great obligations to that gentleman for liberal supplies of specimens for examination.

March 14, 1872.

The EARL OF ROSSE, D.C.L., Vice-President, in the Chair.

The following communications were read :—

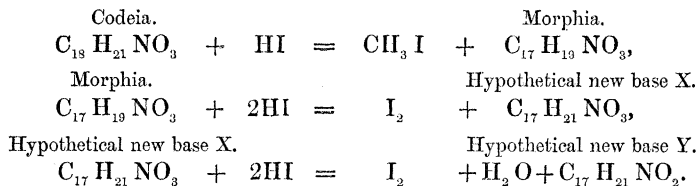
- I. "Contributions to the History of the Opium Alkaloids.—Part IV." By C. R. A. WRIGHT, D.Sc., Lecturer on Chemistry in St. Mary's Hospital Medical School. Received January 29, 1872.

§ 1. *On the Action of Hydriodic Acid on Morphia in presence of Phosphorus.*

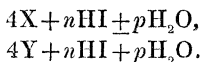
It has been shown in Part III. of these researches* that when hydriodic acid acts on codeia in presence of phosphorus, a series of products are ulti-

* *Suprà*, p. 8.

mately obtained which may be considered as formed by the following train of reactions :—



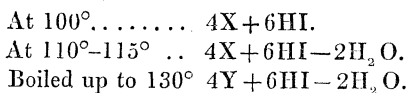
These two hypothetical bases, X and Y, then serve as the foundations of two series of new products expressible by the general formulæ :—



In accordance with these views, it might be anticipated that, on treating morphia with hydriodic acid and phosphorus, either the same products, or at least products belonging to these same series, would ultimately result, which is in fact the case.

The morphia used in these experiments was presented for the purpose by Messrs. Macfarlane of Edinburgh, to whom the writer has already been so much indebted for similar acts of liberality ; the hydriodic acid was prepared as described in Part III., and contained 50 to 55 per cent. of HI.

On dissolving morphia by the aid of heat in about four times its weight of this acid, a marked brown coloration is visible, indicating the separation of iodine ; on adding phosphorus and continuing to heat, this colour ultimately disappears, a colourless syrupy liquid being obtained, which is freed from amorphous phosphorus and the phosphorus acids produced during the reaction by filtration through asbestos while hot, precipitation by water &c., precisely as in the case of the similar codeia products. On thus treating codeia, one or other of three products appear to be formed, according to the temperature employed, viz. :—



In the case of morphia, however, the resulting product is the same at whatever of these temperatures the reaction ensues, and has the composition $4\text{X} + 6\text{HI} - 2\text{H}_2\text{O}$. Thus the following numbers were obtained after complete drying at 100° :—

(A) Digested four hours at 100° .

0.3695 grm. gave 0.5920 CO_2 and 0.1710 H_2O .
 0.3325 „ 0.2410 AgI.

(B) Gently boiled ten minutes.

0.3955 grm. gave 0.6240 CO_2 and 0.1770 H_2O .
 0.3465 „ 0.2530 AgI.
 0.4420 „ 0.3260 AgI.

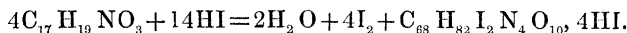
(C) Boiled till the thermometer stood at 132°.

0·3150 grm. gave 0·4990 CO₂ and 0·1400 H₂ O.

0·4405 „ 0·3280 AgI.

	Calculated.		Found.			Mean.
	A.	B.	C.			
C ₆₈	816	43·40	43·69	43·03	43·20	43·31
H ₈₆	86	4·58	5·14	4·97	4·94	5·02
I ₆	762	40·53	39·17	39·46	39·86	39·68
N ₄	56	2·98				
O ₁₀	160	8·51				
C ₆₈ H ₈₂ I ₂ N ₄ O ₁₀ , 4HI	1880	100·00				

Hence this product is formed from morphia in accordance with the equation



In physical properties and qualitative reactions the substance thus got is indistinguishable from the product of the same composition obtained from codeia; like the codeia product, too, it loses the elements of HI on long-continued boiling with water.

§ 2. Action of Water on the foregoing Compounds.

When the original substance C₆₈H₈₂I₂N₄O₁₀, 4HI is boiled for five hours with about three hundred times its weight of water, a liquid is obtained from which white flakes separate on cooling; these have the same curious microscopical structure as the body similarly obtained from codeia, and gave the following numbers after drying at 100°:—

0·3680 grm. gave 0·6220 CO₂ and 0·1770 H₂ O.

0·4240 „ 0·7165 CO₂ and 0·2050 H₂ O.

0·3780 „ 0·2520 AgI.

	Calculated.		Found.	
C ₆₈	816	46·58	46·10	46·09
H ₈₅	85	4·85	5·34	5·37
I ₅	635	36·24		36·02
N ₄	56	3·20		
O ₁₀	160	9·19		
C ₆₈ H ₈₁ I N ₄ O ₁₀ , 4HI	1752	100·06		

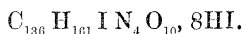
Hence this substance is formed by the reaction



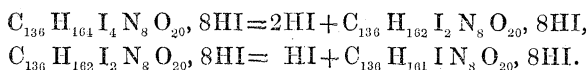
identical with that which takes place with the corresponding compound in the codeia series.

When the compound C₆₈H₈₁IN₄O₁₀, 4HI from codeia is further treated

with excess of water and boiled for several hours, a further elimination of the elements of HI has been shown to take place, the end product having the composition $C_{68}H_{80}N_4O_{10}, 4HI$; as stated in Part III., however, it is very difficult to push this reaction to its extreme. Precisely the same facts are observable with the above morphia product; by boiling this with three hundred times its weight of water for three hours, half the basic iodine it contains is eliminated as HI, forming a product which may be either a mixture of equivalent quantities of $C_{68}H_{81}IN_4O_{10}, 4HI$ and $C_{68}H_{80}N_4O_{10}, 4HI$, or a single substance of the formula



If this latter be the case, the formulæ hitherto attributed to the derivatives from codeia and morphia obtained by the action of III are only half the true ones; and the formation of this substance may be expressed by the equations



The following considerations tend to show that this body is a single substance and not a mixture:—

1st. By treating the compound hitherto described as $C_{68}H_{81}IN_4O_{10}, 4HI$ from codeia with water, a body which has the composition of



is produced previously to the production of the substance hitherto described as $C_{68}H_{80}N_4O_{10}, 4HI$. Now it is not probable that in two separate instances *one* compound should split up into mixtures of *two* bodies of analogous though slightly different constitutions, these two being formed in each case in *equivalent quantities*.

2nd. A body which is without doubt a single compound, and which has the formula $C_{136}H_{153}IN_8O_{20}, 8HI$, has been produced (as will be described in a subsequent communication) by the simultaneous action of HI and P on a polymeride of codeia obtained from that base by the action of phosphoric acid: in physical and chemical properties this product much resembles the two bodies thus obtained from morphia and codeia products by the action of water; and hence these two bodies probably contain, like it, C_{136} associated with I in the base.

In order to show the resemblance between, or rather the identity of the codeia and morphia products, the formulæ given in Part III. have been adopted in this paper (viz. those containing C_{68}); but the author has no doubt that each of the substances has really double the formula ascribed to it (*i. e.* that each contains C_{136}).

The substances of composition $C_{136}H_{161}IN_8O_{20}, 8HI$ obtained, as above-mentioned, from codeia and morphia products by the continued action of water gave the following numbers on analysis after drying at 100° :—

A. Codeia product, 0·3985 grm. gave 0·7050 CO₂ and 0·200 H₂ O.

0·3670 „ 0·2280 AgI.

B. Morphia product, 0·3190 „ 0·5635 CO₂ and 0·1610 H₂ O.

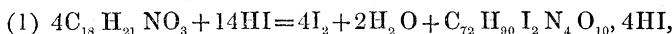
0·3140 „ 0·5560 CO₂ and 0·1570 H₂ O.

0·2840 „ 0·1775 AgI.

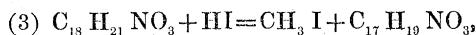
	Found.				
	Calculated.		A.	B.	
C ₁₃₆	1632	48·34	48·25	48·17	48·29
H ₁₆₉	169	5·01	5·55	5·61	5·55
I ₉	1143	33·86	33·57	33·77	
N ₈	112	3·31			
O ₂₀	320	9·48			
C ₁₃₆ H ₁₆₁ I N ₈ O ₂₀ , 8HI	3376	100·00			

In physical character and chemical deportment the derivatives from morphia obtained as above described are indistinguishable from those of the same composition obtained from codeia. The physiological experiments of Mr. Stocker given in the next section show that no particular difference is discernible in this respect also ; hence it is concluded that the codeia products are not merely isomeric, but are identical with the corresponding morphia derivatives.

From the fact that hydriodic acid alone does not eliminate methyl from codeia in the form of methyl iodide, but causes the separation of free iodine, it appears more probable that the formation of the compound C₆₈ H₈₂ I₂ N₄ O₁₀, 4HI, obtained by the action of hydriodic acid in presence of the phosphorus on codeia, is brought about in accordance with the equations :—



rather than the equations



i. e. that the action does *not* consist in the production of morphia from codeia and its subsequent alteration by addition of H₂, polymerization, addition of 2HI, and subtraction of 2H₂O ; but that these alterations take place in the codeia molecule before the elimination of methyl as CH₃I, this elimination forming the last stage instead of the first. This circumstance may account for the non-production from morphia of compounds belonging to the series 4Y + *n*HI ± *p*H₂O, which are formed from codeia when the temperature of the reaction reaches 130°, and under other circumstances ; for it might naturally be expected that the elimination of the

methyl group would place a portion of the molecule in a quasi-nascent condition, thereby rendering further changes more easy.

The foregoing experiments, taken into consideration together with those formerly obtained in conjunction with the late Dr. Matthiessen*, lead to several noteworthy conclusions and speculations.

(1) The actions of hydrochloric, hydrobromic, and hydriodic acids on morphia and codeia are not precisely analogous; thus the action of HCl appears to give rise more especially to products derived from non-polymerized bases; *e. g.*, chlorocodide, which regenerates ordinary codeia by the action of water†. By the action of HBr, codeia yields not only bases apparently formed from non-polymerized codeia (bromocodide, deoxycodide, deoxymorphia), but also bases derived from polymerized codeia and accordingly containing at least C_{72} , and probably C_{144} (chloro- and bromotetracodeia). Hydriodic acid, on the other hand, yields no body whose formula can be written as containing less carbon than C_{34} ; and from the physical characters of the first products of the action and the constitution of their derivatives (many of which contain at least C_{68} and some apparently C_{136}), this proportion of carbon must certainly be doubled and probably quadrupled.

Hence HCl yields single-molecule derivatives chiefly; HBr yields single-molecule derivatives, and also polymeride derivatives, the polymerides containing at least C_{68} or C_{72} (possibly the formulæ attributed to bromotetracodeia and analogous bases may require doubling, as the physical character of the bases and their salts indicate that they belong to the same rank as the iodine derivatives); HI yields polymeride derivatives only.

(2) It being assumed that the molecules of codeia and morphia contain respectively either C_{18} and C_{17} or C_{36} and C_{34} (which latter is probably the case, experiments now in progress indicating that the molecular formulæ of these bases are double those usually ascribed to them), the above experiments lead to the conclusion that there exist polymerides of these alkaloids containing C_{72} , C_{144} , ... , or C_{68} , C_{136} , ... , these polymerides being formed by the action of strong acids, and serving as starting-points for new series of derivatives. Experiments to obtain these polymerides in an unaltered condition are, as has been previously stated, in progress, and apparently with success.

This facile disposition to form polymerides is not an unknown feature in alkaloids, the experiments of Anderson having shown that the pyridine bases are characterized by this property. This fact would appear to warrant the speculation that morphia and codeia contain carbon groups analogous

* Matthiessen and Wright, Proc. Roy. Soc. vol. xvii. pp. 455, 460; and vol. xviii. p. 83.

† Experiments are in progress which appear to show that the action of HCl on both codeia and morphia is capable of giving rise, when pushed to an extreme, of bases insoluble in ether, and of characters similar to chloro- and bromo-tetracodeia, with less ease, however, than HBr.

(5) It appears not improbable that codeia and morphia may contain in their molecules benzene residues. Schiff has pointed out* that phenols give colorations with ferric chloride, whereas the corresponding ethers or anisols do not do so; the well-known distinction between morphia and codeia in this respect, therefore, gives some support to the idea that both may be benzene derivatives.

§ 3. *On the Physiological Action of some of the foregoing Derivatives.*
By REGINALD STOCKER, M.B., Pathologist in St. Mary's Hospital Medical School.

Doses of 1 decigramme of the compound $C_{68}H_{81}IN_4O_{10}$, 4HI from codeia, and of the similar compound from morphia, were given to an adult terrier by the mouth without producing any perceptible effect whatever; when the dose was increased to 3 decigrammes, in each case repeated defæcation in the course of a few hours was produced, the stools being more loose than ordinarily and frequently of a dark greenish colour; no other symptom was noticeable, and no appreciable difference in the action of the two compounds was perceptible.

Doses of 5 decigrammes of the compound $C_{68}H_{82}I_2N_4O_{10}$, 4HI from each of these sources were given to the same dog by the mouth, with the result of producing similar repeated defæcation in the course of two or three hours; the sole difference discernible between these and the former experiments being that the effect was produced somewhat sooner and was of longer continuance in the latter cases, a result probably produced solely by the larger dose. No material differences were observed between the codeia and morphia derivative.

The same dog was employed throughout, two or three days being allowed to intervene between each experiment, so that the animal had recovered from the effects of a former dose before the administration of another.

It would hence appear that the derivatives of polymerized $C_{17}H_{21}NO_3$ are less active than those of polymerized $C_{17}H_{19}NO_3$; and also that there is no reason for considering the derivatives from codeia as different from those of morphia, the corresponding bodies having respectively the same quantitative composition and the same physical, chemical, and physiological properties.

II. "Further Investigations on Planetary Influence upon Solar Activity." By WARREN DE LA RUE, D.C.L., F.R.S., BALFOUR STEWART, LL.D., F.R.S., and BENJAMIN LOEWY, F.R.A.S. Received January 30, 1872.

1. In a previous communication by us to this Society, an Abstract of which was published in the Proceedings, vol. xiv. p. 59, we showed some

* Ann. Chem. Pharm. vol. clix. p. 158.